RESEARCH PAPERS

Comparison of Flavor Thresholds of Aliphatic Lactones with Those of Fatty Acids, Esters, Aldehydes, Alcohols, and Ketones [1,2]

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Abstract

Taste thresholds at 50% detection of 10 of the more prevalent naturally occurring γ- and δ-lactones were measured in water. Several lactone thresholds were determined in deodorized butter oil. Water thresholds of the lactones were compared with those of homologous series of ethyl esters, methyl ketones, free fatty acids, aldehydes, and alcohols. Relatively low thresholds were observed for γ-lactones, and for some of the esters and aldehydes.

Introduction

The aliphatic γ- and δ-lactones occur naturally in many food products. Keeney and Patton in 1956 (16) first isolated δ-decalactone from heated milk, and demonstrated it in evaporated milk, dried cream, and dried whole milk. It has been reported that lactones increase during processing of raw milk for various dairy products (17, 28). Dimick et al. (7) found δ-lactones in several animal fats, and lactones have been reported in autoxidized vegetable oils (8). Gamma- and δ-lactones also have been reported in apricots (26), peaches (26), pineapples (26), raspberries (22), and coconuts (1).

While lactones have been implicated in off-flavors of dairy products (16, 25), they also contribute desirable flavors to products such as butter (6). Several patents have been acquired for adding various lactones to margarine (4, 5, 27).

The purpose of this paper is to report more data on the flavor intensities of common γ- and δ-lactones, and to compare them with the flavor intensities of compounds in other aliphatic classes.

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Experimental Methods

Compounds used in this study and purified to more than 99.8% by methods previously reported (23) are as follows:

γ-Lactones
- Hexalactone
- Heptalactone
- Octalactone
- Nonalactone
- Decalactone
- Undecalactone

Ethyl esters
- Formate
- Acetate
- Butyrate
- Hexanoate
- Octanoate
- Decanoate
- Dodecanoate

Normal methyl ketones
- Acetone
- 2-Butanone
- 2-Pentanone
- 2-Hexanone
- 2-Heptanone
- 2-Octanone
- 2-Nonanone
- 2-Decanone
- 2-Undecanone
- 2-Tridecanone

δ-Lactones
- Octalactone
- Decalactone
- Dodecalactone
- Tetradecalactone

Normal aldehydes
- Pentanal
- Hexanal
- Heptanal
- Octanal
- Nonanal
- Decanal
- Undecanal
- Dodecanal

Normal 2-alkanols
- 2-Propanol
- 2-Butanol
- 2-Pentanol
- 2-Hexanol
- 2-Heptanol
- 2-Nonanol
- 2-Decanol

Fatty Acids
- Acetic
- Butyric
- Hexanoic
- Octanoic
- Decanoic

Normal alkanols
- Ethanol
- 1-Propanol
- 1-Butanol
- 1-Pentanol
- 1-Hexanol
- 1-Heptanol
- 1-Nonanol
- 1-Decanol

TABLE 1. Taste thresholds of γ- and δ-lactones in water and deodorized butteroil.

Carbon number	Threshold in water[a]		Threshold in oil	
	Gamma	Delta	Gamma	Delta
	(ppm)			
6	13.0	—	8.0	—
7	0.52	—	3.4	—
8	0.095	0.57	3.5	3.0
9	0.065	—	2.4	—
10	0.088	0.16	1.0	1.4[b]
11	0.025	—	0.93	—
12	——	0.10	—	95.0
14	——	9.8	—	500.0

[a] Keith et al. (15) reported 0.40, 0.090, and 0.15 ppm for the gamma-C_8-, C_{10}-, C_{11}-lactones and 1.0 ppm for delta-dodecalactone.
[b] From Siek et al. (23).

Slightly water soluble lactones, generally those with more than 5 carbons, were dissolved in aqueous solutions by the method of Guadagni et al., (9). The compound was first dissolved in ethanol and then diluted with water to the desired concentration. The ethanol after dilution was below 70 ppm, which in our studies was sub-threshold.

Details of conducting the taste tests in both water and deodorized butteroil have been given (23). Prior to determination of taste thresholds by a 20-member panel, one or more preliminary tests were conducted to find approximate thresholds. Thresholds were obtained by plotting positive responses (panelist could taste compound) against concentration. The concentration at which 50% of the panel detected the compound (uncorrected for chance level expectation) was designated the taste threshold (21). Preliminary studies showed that consistent results could be obtained by testing over a 10- to 40-fold range between the high and low concentration samples.

Results

Thresholds for 2 homologous series of lactones in water and oil are in Table 1. The data show that chain length being equal, oil thresholds are higher than water thresholds (an exception is γ-hexalactone), and that detection thresholds in water for γ-C-8 and -C-10 lactones were lower than for the δ-C-8 and -C-10 lactones. Reproducibility was ascertained by repeating 2 or 3 times (not counting preliminaries), tests of 12 compounds which had low thresholds. The normalized standard deviation was 1.00 ± 0.17; thus the expected standard deviation for a given threshold in Table 1 would be approximately ± 17%.

Results of threshold measurements by the 20-memebr panel for some aliphatic compounds other than lactones are in Table 2. Values from the literature are included in Table 2 for a more complete evaluation.

TABLE 2. Taste thresholds of several classes of normal aliphatic volatile compounds in water—50% detection level.

Carbon	Ethyl esters	Free fatty acids	Normal aldehydes	Normal alkan-2-ones	Normal alkanols	Normal alkan-2-ols
	(ppm)					
2	—	22	1.2[b]	—	200	—
3	6.6[a]	—	0.43[b]	450	45	190
4	6.6	6.2	0.19[b]	60	7.5	5.1
5	—	—	0.070	2.3	4.5	8.5
6	0.015	15	0.015	0.93	2.5	6.7
7	—	—	0.031	0.65	0.52	0.41
8	0.012	5.83	0.047	0.15	—	—
9	—	—	0.045	0.19	0.086	0.28
10	0.032	3.5[c]	0.010	0.19	0.18	0.33
11	—	—	0.014	0.45	—	—
12	0.49	—	0.011	—	—	—
13	—	—	—	0.50	—	—
14	0.33	—	0.06[d]	—	—	—

[a] Ethyl formate (all C atoms numbered, i.e., C_6 is ethyl butyrate).
[b] From Honkanen et al. (11) in milk. Their value for pentanal was 0.13.
[c] From Patton (20); his values for butyric and caproic acids were 6.8 and 5.4.
[d] From Lea and Swoboda (18).

Discussion

Often close agreement of flavor thresholds between laboratories is not achieved, since each panel conducts flavor tests under different conditions. The flavor potency of lactones in Table 1 may be compared directly with several types of nonlactones in Table 2, since the compounds were evaluated similarly.

Water thresholds of our 4 lactones have been reported by Keith et al., (15). With the exception of γ-decalactone, their values are from 4 to 10 times greater. These differences are probably due to differences in testing procedures and evaluation of results. The quantitative literature values for lactones in milk fat are summarized in Table 3. The lactone levels reflect prior heat treatments of the milk fat samples, and thus represent a potential concentration range in milk fat. Comparing the data in Table 3 with those in Table 2, it is evident that several of the γ- and δ-lactones should be important in milk fat flavors. The lactones would be especially important if significant flavor interactions were involved.

The lower taste thresholds in water compared with oil observed in our study have been reported by Patton (20) and by Lea and Swoboda (18). Odor thresholds, expressed in parts per million of dissolved odorant, also depend on the solvent used. Jellinek (13) noted a solvent effect with perceived odors; he discussed his findings in terms of intermolecular dipole-dipole, induction, and London dispersion forces between solvent and odorant. The rate of diffusion of odorant molecules to the surface to replace evaporated molecules (considering an open system) would be of primary importance in very dilute solutions. This diffusion rate would be considerably lower in highly viscous butteroil than in water. The rate of evaporation of odorant in water would depend primarily on intermolecular hydrogen bond strengths; in oil other intermolecular interactions (dipole-dipole, induction, and London forces) in addition to hydrogen bonds would retard evaporation.

Table 4 lists several compounds by volatility with their respective thresholds. Vapor pressure data in Table 4 were compiled from the *Handbook of Chemistry and Physics* (10), the *International Critical Tables* (12), and Othmer et al. (19). Boiling points of γ-valero-, γ-capro- and γ-decalactone and δ-tetradecalactone have been reported (3, 10, 11). With these lactones as references, boiling points of other lactones were estimated from gas chromatographic data on Apiezon M. It was noted on this column that the boiling point was proportional to the log retention time for each of the different homologous series. Latent heats of vaporization for lactones were also estimated. The order of compounds in Table 4 (in order of decreasing vapor pressure) would not be significantly changed by possible errors in the estimates.

TABLE 3. Summary of reported concentrations of γ- and δ-lactones in milk fat.

Carbon number	Lactone in milk fat: Jurriens and Oele (14)	Kinsella et al. (17)	Siek and Lindsay (24)
	(ppm)		
Gamma-			
10	0.6	1.2	0.10
11	0.2	0.5	0.05
12	1.8	1.6	0.3
Delta-			
8	—	2.6	0.40
10	9.0	15.0	2.0
11	0.6	0.7	0.10
12	28.5	35.0	5.0
14	21.5	34.0	4.0

TABLE 4. Vapor pressures and thresholds of various normal aliphatic compounds containing from 6 to 14 carbon atoms.

Compound	Vapor pressure at 40C	Threshold[a]
	(mm Hg)	(ppm)
Ethyl caproate	6.6	0.012
n-Octanal	5.5	0.047
n-Hexanol	3.3	2.5
2-Octanone	2.9	0.15
Ethyl caprylate	1.6	0.032
2-Nonanol	0.78	0.28
2-Decanone	0.74	0.19
γ-Caprolactone	0.50	13.0
n-Decanal	0.46	0.010
Ethyl caprate	0.30	0.49
n-Nonanol	0.24	0.086
γ-Octalactone	0.11	0.095
δ-Octalactone	0.072	0.57
γ-Nonalactone	0.052	0.065
2-Tridecanone	0.031	0.50
n-Tetradecanal	0.030	0.06
γ-Decalactone	0.017	0.088
δ-Decalactone	0.012	0.16
δ-Dodecalactone	0.002	9.8

[a] Thresholds from Tables 1 and 2.

The data in Table 4 show, in agreement with many previous publications, that no simple relationship exists between flavor thresholds and volatility. For comparable vapor pressures, aldehyde thresholds are much lower than methyl ketone thresholds. Assuming the carbonyl group interacts with the receptor, steric effects must be considered in comparing an aldehyde and a methyl ketone. Ring size in relation to receptor site fit might explain γ- and δ-lactone threshold differences. The disparity between thresholds of ethyl esters and lactones, which are internal esters, at comparable vapor pressures further emphasizes that molecular size and stereochemistry can be important, as indicated by Amoore (2).

References

(1) Allen, R. R. 1965. Volatile flavor constituents in coconut oil. Chemistry and Industry, Sept. 4, p. 1560.

(2) Amoore, J. E. 1967. Stereochemical theory of olfaction. Chemistry and Physiology of Flavors. Shultz, H. W., E. A. Day, and L. M. Libbey, ed. AVI Publishing Co., Inc. Westport, Connecticut.

(3) Bedoukian, P. Z. 1967. "Perfumery and Flavoring Synthetics." Elsevier Publishing Co. New York, New York.

(4) Boldingh, J., P. H. Begemann, G. Lardelli, R. J. Taylor, and Wm. T. Weller. Lactones for flavoring margarine. Patent to Unilever Ltd., Great Britain 748661. May 9, 1956.

(5) Boldingh, J., and R. J. Taylor. Flavoring of oleaginous foods. Patent to Lever Bros. Co., U.S. 2819168. January 7, 1958.

(6) Boldingh, J., and R. J. Taylor. 1962. Trace constituents of butterfat. Nature, 194: 909.

(7) Dimick, P. S., S. Patton, J. E. Kinsella, and N. J. Walker. 1966. The prevalence of aliphatic delta-lactones or their precursors in animal fats. Lipids, 1: 387.

(8) Fioriti, J. A., V. Krampl, and R. J. Sims. 1967. Lactones in autoxidized vegetable oils. J. Amer. Oil Chemists' Soc., 44: 534.

(9) Guadagni, D. G., R. G. Buttery, and S. Okano. 1963. Odor thresholds of some organic compounds associated with food flavors. J. Sci. Food Agr., 14: 761.

(10) Handbook of Chemistry and Physics. 1958. Chemical Rubber Publishing Co., Cleveland, Ohio.

(11) Honkanen, E., P. Karvonen, and A. I. Virtanen. 1964. Studies on the transfer of some flavor compounds to milk. Acta Chem. Scand., 18: 612.

(12) "International Critical Tables." 5. 1929. Washburn, E. W. ed. McGraw-Hill Book Co., Inc. New York, New York.

(13) Jellinek, J. S. 1964. The effect of intermolecular forces on perceived odors. Ann. New York Acad. Sci. 116: 725.

(14) Jurriens, C., and J. M. Oele. 1965. Determination of hydroxyacid triglycerides and lactones in milk. J. Amer. Oil Chemists' Soc., 42: 857.

(15) Keith, Elizabeth S., and John J. Powers. 1968. Determination of flavor threshold levels and sub-threshold, additive, and concentration effects. J. Food Sci., 33: 213.

(16) Keeney, P. G., and S. Patton. 1956. The coconut-like flavor defect of milk fat. Isolation of the flavor compound from butteroil and its identification as delta-decalactone. J. Dairy Sci., 39: 1104.

(17) Kinsella, J. E., S. Patton, and P. S. Dimick. 1967. The flavor potential of milk fat. A review of its chemical nature and biochemical origin. J. Amer. Oil Chemists' Soc., 44: 449.

(18) Lea, C. H., and P. A. T. Swoboda. 1958. The flavor of aliphatic aldehydes. Chem. and Ind., p. 1289.

(19) Othmer, D. G., P. W. Maurer, C. J. Molinary, R. C. Kowalski. 1957. Correlating vapor pressure and other physical properties. Ind. and Eng. Chem., 49: 125.

(20) Patton, S. 1964. Flavor thresholds of volatile fatty acids. J. Food Sci., 29: 679.

(21) Patton, S., and D. V. Josephson. 1957. A method for determining significance of volatile compounds in Foods. Food Res., 22: 316.

(22) Schinz, H., and C. F. Seidel. 1957. Aromatic materials. I. Raspberry aromatic materials. Helv. Chim. Acta, 40: 1839. (Chem. Abstr., 52: 3270 (1958).

(23) Siek, T. J., I. A. Albin, L. A. Sather, and R. C. Lindsay. 1969. Taste thresholds of butter volatiles measured in butteroil. J. Food Sci., 34: 265.

(24) Siek, T. J., and R. C. Lindsay. 1970. Semi-quantitative analysis of fresh sweet cream volatiles. J. Dairy Sci., 53: 700.

(25) Tamsma, A., F. E. Kurtz, A. Konstan, and M. J. Pallansch. 1969. Organoleptic properties and gas chromatography patterns of steam distillates from fresh and stale milk fat. J. Dairy Sci., 52: 152.

(26) Tang, C. S., and W. G. Jennings. 1968. Lactonic compounds of apricot. J. Agr. Food Chem., 16: 252.

(27) Wode, N. G., and U. Holm. Aromatizing margarine and other fat-containing foods. Margarinbolaget AB Sweed. 188224, March 17, 1964.

(28) Wyatt, Jane C., R. L. Pereira, and E. A. Day. 1967. Lactone precursor in fresh milk fat. Isolation and characterization of the precursor. J. Dairy Sci.. 50: 1760.